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Computer simulations of extractant primary amine N1923 and N1923 hydrochloride salt at water/chloroform interface

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A molecular dynamics (MD) simulation has been carried out to investigate the structural and dynamical properties of extractant methyloctadecyl amine (N1923), and its hydrochloride salt at water/chloroform interface. The simulation results show that both N1923 molecule and protonated N1923 ion can self-assembly form a monolayer at the interface like most non-ionic or cationic surfactants. It is not only observed that the headgroup N atom of protonated N1923 ion arranges more tightly and orderly than that of N1923 molecule but also verified that the protonated headgroup of N1923 ion has stronger hydration ability than the polar headgroup of N1923 molecule.

Keywords: Molecular dynamics; Liquid/Liquid interface; Monolayer; Primary amine N1923

1. Introduction

Amine extractants are often used to extract a variety of metal ions from acidic aqueous media [1–4]. Both amine molecules and their salt ions have amphiphilicity in various systems. Therefore, the existent state or structural characteristics of amine extractants, as well as their succeeding reactions with metal ions at the liquid–liquid interface are primarily important processes in the solvent extraction of metal ions. However, the mechanism of reactions at the interface is still less understood than that in bulk solution, because of the lack of information on solvent structure of the interface and the molecular configuration of the adsorbed extractant.

The interface of extraction system is usually studied by measuring the interfacial tension, viscosity and potential. Spectroscopic methods, such as X-ray and neutron reflectivity, are also used to provide structural insights into molecules adsorbed at interface, but data related to ion extraction systems are relatively scarce. Computer simulation is another promising approach to study the structure of liquid–liquid interfaces. In the last decade, molecular dynamics (MD) and Monte Carlo (MC) simulations have been used to study the interfacial behaviors and provided microscopic morphology in solution [5–11].

N1923, $C_{17}H_{35}CH(CH_3)NH_2$, is an important extractant of primary amine with a long hydrocarbon chain synthesized in China. N1923 molecule or acidified N1923 cation (for example, $C_{17}H_{35}CH(CH_3)NH_3Cl$) can be considered as a non-ionic or cationic surfactant. Up to now, we have reported some properties of N1923, such as its interfacial properties in different diluents [12], the microstructure studies of primary amine N1923/*n*-heptane/alcohol/water reverse micelles [13] and its pocket effect of extraction of iron (III) from sulphuric acid solution [3]. Herein, we investigate the behaviors of neutral N1923 and its acidified hydrochloride salt in the water/chloroform system using MD simulation.

2. Model and methods

The initial configuration was prepared as follows. Firstly, we constructed two amorphous cells containing 900 water molecules and 200 chloroform molecules, in which both the lengths of *x*- and *y*-axis were 30 Å and the densities were 0.997 or 1.49 g/cm³ for water and chloroform at room temperature for the experiments, respectively. In order to see the insights of how the N1923 molecules or protonated N1923 ions are oriented and ordered at the water/chloroform interface, then the initial configuration

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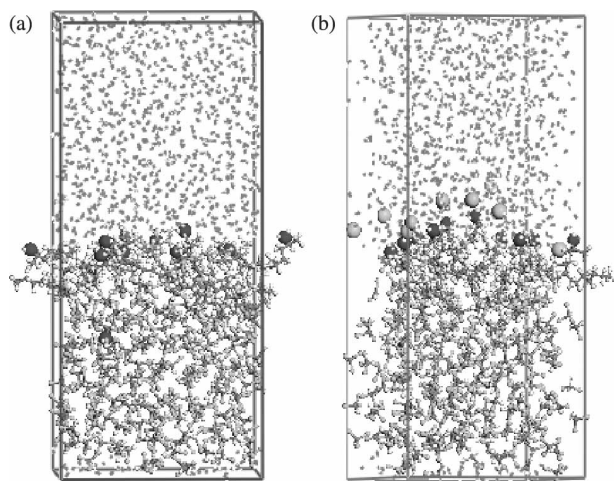


Figure 1. Snapshots of the configurations of N1923 molecule (a) and N1923 hydrochloride salt (b) at the CHCl_3 /water interface at the end of the simulation. For visual clarity, the nitrogen atoms and the chloride counterions are drawn as van der Waals spheres, water molecules are drawn by line style in red color and chloroform molecules are drawn by stick-ball style in green color.

of 10 N1923 molecules or its hydrochloride salts were prepared in a disordered orientation between the liquid/liquid interface. The finally cells were $30 \times 30 \times 68.02$ or 68.15 \AA for N1923 molecule system or its hydrochloride salt system, respectively.

The MD simulations were carried out at NVT ensemble with a time step of 0.001 ps. The temperature was maintained at 298 K using the Andersen thermostat [15] with collision frequency of 1.0 ps. The initial velocity assigned to each atom was chosen from a Maxwell–Boltzmann distribution corresponding to the desired simulation temperature. The periodic boundary condition was applied in all three directions, which resulted in one additional interface (see figure 3). The cell multipole method with update width 1.0 was used to handle non-bond interactions.

After a 1.5 ns, MD equilibration was performed, at least 500 ps MD production was run to obtain the dynamic

information using the trajectory of molecules in the simulation box. The results were analyzed from the coordinates, which were saved every 0.2 ps. COMPASS force field [14] was selected and all the simulations were carried out using the software Cerius² 4.6 by accelrys.

3. Results and discussion

3.1 Configuration, headgroup, and hydrocarbon chain tail (C18) locations

In previous study [12], we know that N1923 molecule can adsorb and presumably form a monolayer at water/chloroform interface from the experiment and a saturation area of N1923 molecule, 98.5 \AA^2 , was calculated. Sometimes the microstructures can give some interaction mechanism and offer new ideas for designing new extracant; therefore, we focus more on the structures of N1923 molecules or its hydrochloride salts in the molecular level at water/chloroform interface. According to the experimental results [12], ten N1923 molecules or N1923 hydrochloride salts, which the systems were corresponding to $90 \text{ \AA}^2/\text{molecule}$, were put at the water/chloroform interface with a disordered orientation. At the end of simulations, two different morphologies are found for the two systems. For N1923 molecule system (figure 1(a)), nine N1923 molecules form a monolayer with their polar amino groups close to the aqueous phase of the interface and long hydrocarbon chains immersed in organic phase, only one N1923 molecule migrated to the chloroform phase. However, for N1923 hydrochloride salt system (figure 1(b)), all ten protonated N1923 ions adsorb at the interface and form a monolayer with protonated amino groups immersed in water phase and long hydrocarbon chains remaining in chloroform phase to exhibit stronger interfacial activity. Especially, around the headgroup N atoms, chloride ions are found, and are all located in water phase.

The Z-dependent density distribution profiles (figure 2) show that N1923 molecules or ions mainly distribute in the interfacial area and the neutral N1923 molecules are

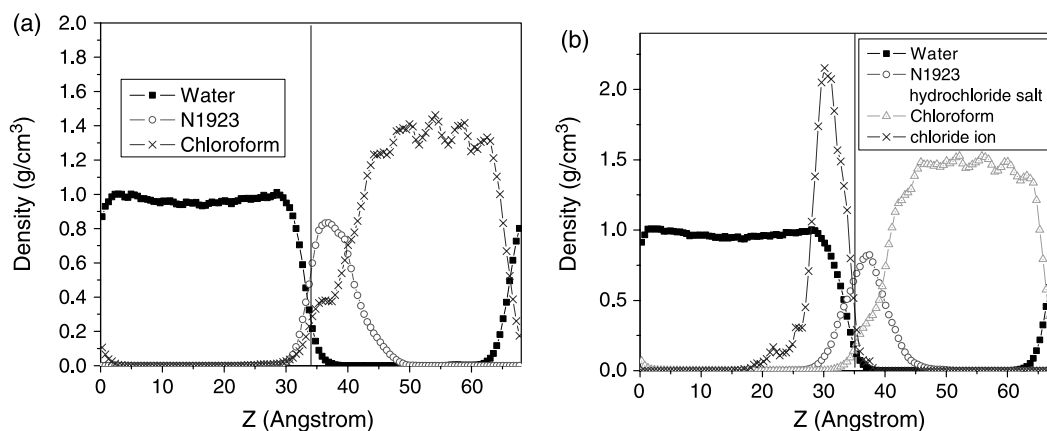


Figure 2. Density profiles for the N1923 molecule (a) and N1923 hydrochloride salt (b) at the CHCl_3 /water interface.

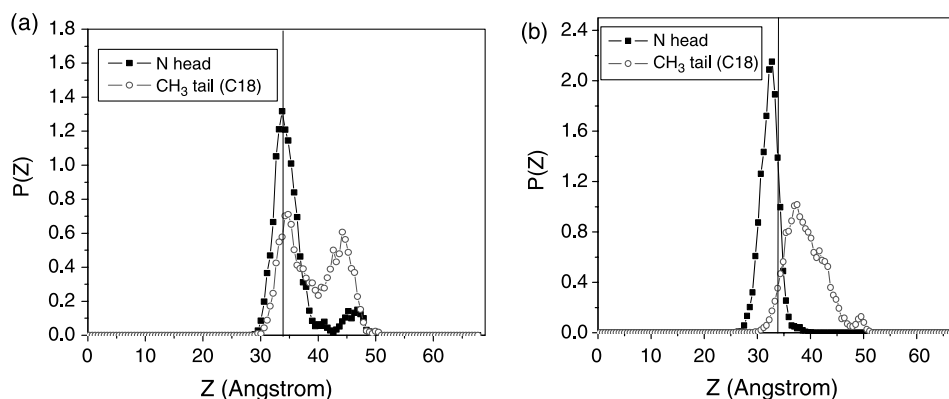


Figure 3. Z-dependent probability distributions for the headgroup N atom and CH₃ tail (C18) in the N1923 molecule (a) and N1923 hydrochloride salt (b) systems. (The middle dark line represents the position of the interface.)

attracted a little more by chloroform than by water in comparison with N1923 hydrochloride salts.

Apparently, the main features are in good agreement with the well-known picture of surfactant organization at liquid/liquid interface: the headgroups are located at the interface, the hydrophobic tails are mostly excluded from the water phase and counterions are largely associated with the cationic headgroups in the water phase. We think that besides the hydrophobic interaction, the electrostatic interaction between the headgroups and chloride ions are also very important factor for the structure at water/chloroform interface.

In order to clearly distinguish the location of headgroups of extractant molecules in the two monolayers, individual probability distributions $P(Z)$ for nitrogen atoms in the headgroups and methyl groups (C18) at the end of chains are shown in figure 3, respectively. We notice that for the N1923 molecule system, the distributions of nitrogen atoms in the headgroups much more remain at the center of the interface area ($Z \approx 34.1 \text{ \AA}$) and methyl groups have more broad area. We also find that there are two peaks for methyl groups along the z -axis, one is located in the area between two phases, the other is located in the chloroform phase.

However, for N1923 hydrochloride salt system, we notice that the distributions of the protonated headgroups are more regularly located in the water phase and the methyl groups are mainly immersed in the chloroform phase. This obviously indicates that acidified N1923, as a cationic surfactant, is more hydrophilic than neutral N1923 molecule. Thus, the strong interactions between protonated headgroups and water molecules, also including chloride counterions, result in that protonated N1923 ions arrange themselves more tightly at the waterside near the interface than N1923 molecules.

In figure 4, we compared the orientation of the hydrophobic hydrocarbon chain (from carbon 1 to carbon 5) by examining the length distribution between the headgroup N atom and C1 to C5 in the hydrocarbon chain (figure 4). For the N1923 molecule system, the doublet peaks appear at the C3–C5, in comparison, the

doublet peaks appear at the C4 and C5 in N1923 hydrochloride salt system. This result also illustrates that the hydrocarbon chain from N atom to C5 of protonated N1923 ion arranges more tightly and orderly at the interfacial area. From figure 1, we can see that with the increase of the distance from the headgroup N atom to each carbon in the chain, the orientation and arrangement of the chains in the chloroform all become somewhat disordered in the two systems.

It is also possible to characterize the distribution of hydrocarbon chain conformations by the probability of gauche defects (figure 5). The dihedral angles are numbered beginning with the N–CH–CH₂–CH₂ fragment (N–C1–C2–C3) and ending with the fragment C15–C16–C17–C18. From this figure, we observe that the N–C1–C2–C3 dihedral (no.1) is always almost *trans* ($\sim 4\%$ gauche), while the following dihedral angle has only about 70% *trans* character in N1923 hydrochloride salt system. In comparison, the N–C1–C2–C3 dihedral is 27% *trans* and the following dihedral angle has only about 60% *trans* character in N1923 molecule system. Why the conformation of the N–C1–C2–C3 dihedral is so different in the two systems? It is known that water

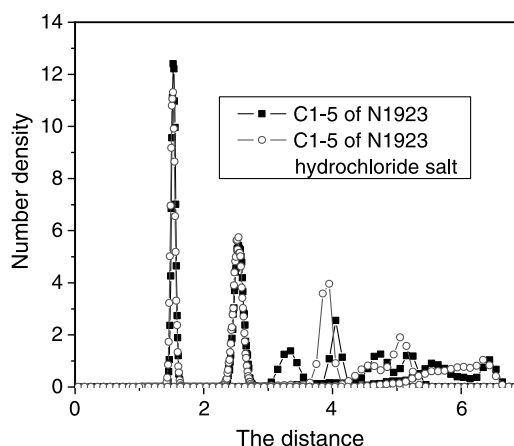


Figure 4. Number density profile of the hydrocarbon chain individual methyl(ene) groups (C1–C5) normal to the interface with respect to the headgroup N atom position.

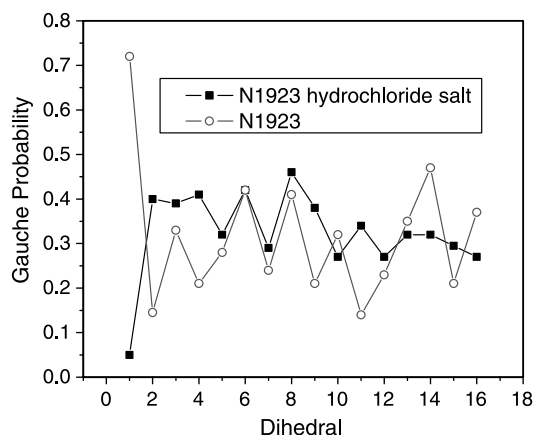


Figure 5. Probability of gauche defects as a function of carbon position.

hydrogen bonding may enhance the N1923 molecules or protonated N1923 ions at the water–chloroform interface. Therefore, it would be more favourable to incorporate the headgroup in a way consistent with minimal disruption of the hydrogen bond network. The different strengths of interactions between the protonated headgroup N atoms or polar headgroup N atoms with water molecules may lead to the different conformations of the N–C1–C2–C3 chains.

3.2 Water structure at the interface

To understand further the properties of an adsorbed N1923 molecule or protonated ion, the structure of water molecules at the interface was investigated using radial distribution function $g(r)$. We have calculated the $g_{\text{NO}}(r)$ of water molecules with N atom of N1923 or N1923 hydrochloride salt, as shown in figure 6. The very sharp first peak in $g_{\text{NO}}(r)$ at 2.75 Å for N1923 hydrochloride salt system suggests that water molecules form a tight first solvation shell around the headgroup, which is expected because of the strong hydrogen bonding between the

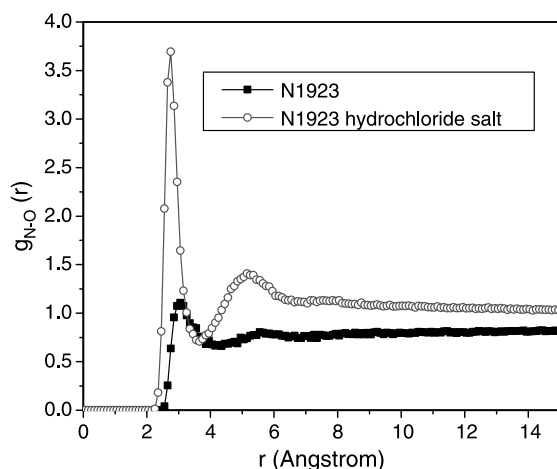


Figure 6. Radial distribution functions, $g_{\text{NO}}(r)$, of the nitrogen (N) atoms of N1923 and N1923 hydrochloride salt with water oxygen atoms.

headgroup and water molecules. The curve also exhibits a well-defined second peak, which indicates a loose second hydration shell. In comparison, the curve of N1923 molecule exhibits a weak first peak and second peak, suggesting that the headgroup N atom is much less exposed to water and thus not as hydrated as the NH_4^+ ion. Integrating up to the first minimum in $g_{\text{NO}}(r)$ gives a coordination number of 5.9 water molecules for protonated N1923 ion and 4.2 water molecules for N1923 molecule in the first hydration shell around the headgroup.

4. Conclusion

We have presented a molecular picture of extractant primary amine N1923 and its hydrochloride salt at the water/chloroform interface. We have shown that both N1923 molecule and protonated N1923 ion can self-assembly adsorb at the interface in a monolayer like most non-ionic and cationic surfactants. In the simulation, the surface coverage of N1923 and protonated N1923 ion is 100 and 90 Å²/molecule, respectively. The structural properties of the two systems, such as the density profiles of different components normal to the plane of the interface and atom probability distributions $P(Z)$ for the headgroup N atoms and the CH_3 (C18) tails are calculated. In N1923 hydrochloride salt system, it is observed that the stronger hydrophilic ability allows the protonated headgroup N atom to insert into the aqueous phase more tightly and orderly nearly perpendicular to the plane of the interface and achieve maximum solvation in comparison with that of N1923 molecule system. We have also investigated the length distribution and dihedral angles. We find that at this surface coverage, the head parts (C1–C5) of the hydrocarbon chain of protonated N1923 ions arrange more orderly than those of N1923 molecules. And except for the probability of gauche defects in the headgroup of N1923 molecules is higher in comparison with that of protonated N1923 ions, the tendency for the dihedral interactions to favor trans conformations is similar in the two systems.

Acknowledgements

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